



Toluene oxidation over ZrO₂-based gasification gas clean-up catalysts: Part A. Effect of oxygen and temperature on the product distribution



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ABSTRACT

Biomass gasification combined with effective gas cleaning is an interesting way to produce energy or syngas for numerous applications. ZrO₂-based catalysts have been proven to remove the undesired tar molecules when a convenient oxygen amount is added. The oxidation of toluene (a tar model compound) was addressed in this work by applying temperature-programmed surface reaction (TPSR) experiments with a continuous feed of toluene and oxygen. Complete toluene conversions were achieved over all zirconia-based catalysts (ZrO₂, Y₂O₃-ZrO₂ and SiO₂-ZrO₂) in toluene oxidation above 550 °C (toluene WHSV 0.06–0.07 1/h). Toluene was oxidized into four products (CO₂, H₂O, CO and H₂). The formation of incomplete oxidation products (CO and H₂) suggests that these catalysts are able to convert undesired tar molecules also into valuable synthesis gas components. Increasing the oxygen amount increased the product ratio of CO₂ and CO. Over pure ZrO₂, the formation of CO and H₂ was detected at 600 °C even with the highest feed ratio of O₂/TOL ($\approx 3.5 \times$ theoretical toluene total oxidation ratio), while over the doped zirconias the formation of CO and H₂ approached zero with increasing temperature and over-stoichiometric feeds. Separate CO oxidation experiments confirmed different but appreciable activities of different zirconia materials for that reaction. However, a very minor water-gas shift activity in the presence of oxygen was detected only over pure ZrO₂ at the studied temperature range. The collected multiresponse reaction data was subsequently subjected to transient kinetic modeling established on hypotheses of surface reaction mechanisms (Part B: Kinetic modeling).

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1. Introduction

Gasification of biomass is an attractive way to produce energy, liquid biofuels via Fischer–Tropsch synthesis as well as numerous chemicals [1]. The main components of gasification gas are CO, H₂ and CO₂ [1]. In addition, the product gas also contains impurities such as ammonia and tar (aromatic hydrocarbons heavier than benzene), and therefore it has to be cleaned before use [2]. One of the most advantageous technologies to decompose the tar molecules is catalytic hot gas cleaning downstream of the gasifier [3,4]. Hence, the activities of several catalysts have been studied in catalytic hot gas cleaning. In a review by Sutton et al., three main types of reforming catalysts for the elimination of tar are listed: dolomite (MgCO₃·CaCO₃), alkali metals and nickel [2].

Over ZrO₂-based catalysts, successful tar decomposition results are obtained when a small oxygen amount is added to the gas, i.e. by selectively oxidizing tar molecules within the gasification gas (e.g.

[5–7]). Reactions involved in the biomass gasification gas cleaning are numerous as equilibrium reactions between the main gas components and hydrocarbon decomposition reactions take place simultaneously, and the addition of oxygen increases the number of possible reactions even further. For this reason, the presence of other gas components (CO, H₂, CO₂, H₂O, etc.) has an effect on the tar oxidation activity of a catalyst [8].

Due to the complexity of the gasification gas mixture, a novel approach was introduced in our previous contribution; the system was simplified to subsystems with fewer components at a time, resulting in an adsorption/oxidation study of a single tar compound (toluene) [9]. In this study, it was discovered by in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) and mass spectrometry that the oxidation of toluene (tar model compound) take place between 300 °C and 600 °C over ZrO₂-based catalysts [9]. Several surface species from toluene were detected; the adsorption of toluene in the absence of gas-phase oxygen resulted in the formation of molecularly adsorbed toluene, surface benzoate species and carbonaceous deposits, whereas in the presence of gas-phase oxygen also surface benzyl species were detected [9]. These surface benzyl species were detected at temperatures where toluene and

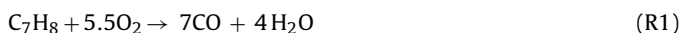
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oxygen started to convert implying that they are the key intermediates in toluene oxidation over ZrO₂-based catalysts [9].

Toluene oxidation has been studied widely in the field of VOC (volatile organic compounds) abatement over several catalysts. An extensive review by Huang et al. [10] on the catalytic oxidation of VOCs includes several noble metal catalysts as well as other transition metal catalysts successfully applied in toluene oxidation. However, compared to gasification gas cleaning, the oxidation of VOCs has a different goal. In gasification gas cleaning the aim is to remove tar molecules while protecting the main gas [4], while in VOC abatement, the goal is the complete elimination of VOCs [10]. Furthermore, the working environments of the catalysts in these two applications differ greatly. For example, toluene conversion of 90% was reported over 0.5 w-% Pd/ZrO₂ at 277 °C in VOC abatement [11] while over 0.5 w-% Pd supported on modified ZrO₂ the temperature needed for the same conversion was 900 °C in gasification gas cleaning [12]. Moreover, it was shown that the addition of metal has a negative effect on the toluene oxidation activity within the gasification gas mixture at temperatures below 800 °C [12]. In addition, a gasification gas clean-up catalyst must protect the valuable components of the main gas, such as CO and H₂.

It was tentatively discovered in our earlier work that over ZrO₂-based catalysts toluene was oxidized into complete oxidation products (CO₂ and H₂O) but also the formation of CO and H₂ was detected [9]. Since CO and H₂ are the main components of the gasification gas, their formation in the oxidation of a tar model compound (toluene) over ZrO₂-based catalysts is highly preferable. This could explain why these catalysts selectively oxidize tar molecules within the gasification gas without altering the main gas. The formation of CO over ZrO₂-based gasification gas clean-up catalysts has been explained by Juutilainen et al. [5] with a two-step toluene oxidation pathway within the gasification gas mixture. First toluene is oxidized into CO and water (Reaction R1) followed by CO oxidation (Reaction R2). In toluene oxidation experiments, the formation of CO over pure and Y₂O₃-doped zirconias has also been reported by Labaki et al. [13]. However, the formation of H₂ was not reported [13]. The origin of H₂ could be a water-gas shift reaction (R3) where the products from reaction R1 react into CO₂ and H₂.



In order to optimize the performance of a tar oxidation catalyst within the gasification mixture and to enable process design ensuring a high-quality product gas, detailed knowledge of the tar oxidation mechanism needs to be established. When ZrO₂-based catalysts are used in catalytic gasification gas cleaning, a small oxygen amount is added. The effect of the amount of added oxygen has not been studied previously. Hence, the aim of this paper is to study how the addition of oxygen affects toluene oxidation over ZrO₂-based catalysts. Special attention was given to the effect of oxygen on the formation of CO and H₂ during toluene oxidation over these catalysts. Thus, toluene oxidation was studied with three O₂-toluene feed ratios in temperature-programmed mode in the temperature range of 200–600 °C. In addition, the possible secondary reactions (CO oxidation and water-gas shift in the presence of oxygen) were studied. The obtained extensive temperature-programmed data was subjected to kinetic modeling in the second part of this study (Part B: Kinetic modeling).

2. Experimental

Pure ZrO₂, 5 mol-% Y₂O₃-ZrO₂ and 8 mol-% SiO₂-ZrO₂ powder samples, supplied by MEL Chemicals, were calcined in static air at

Table 1

Gas mixtures and their purities.

Gas mixture	Purity of reactant gas	Purity of balance gas
He	–	>99.9996%
683 ppm toluene	n.a.	>99.9996%
5.0% O ₂ in He	>99.999%	>99.9996%
0.09% H ₂ O in He	n.a.	>99.9996%

800 °C for 1 h. The physical and chemical characteristics of the catalysts have been reported elsewhere (e.g. [7,9,14]). After calcination, the catalyst samples were pressed into pellets, crushed and sieved to the particle size of 0.25–0.42 mm.

Temperature-programmed experiments were performed in an Altamira AMI-200 R catalyst characterization system and analyzed with an on-line mass spectrometer (Hiden QIC-20). In all of the experiments the same procedure was applied: calcination at 600 °C for 2 h (in 5 vol-% O₂/He), cooling down to 200 °C (in 2.5 vol-% O₂/He), helium flush for 1 h, stabilization under the reaction mixture for 2 h at 200 °C, heating up to 600 °C (10 °C/min) and stabilization for 30 min at 600 °C under the reaction mixture. The sample amount used in each experiment was 100 mg.

In the toluene oxidation experiments, the reaction mixture was obtained by mixing toluene (683 ppm in He with 260 ppm water as impurity) with oxygen (5 vol-% in He). Three feed compositions corresponding to O₂-toluene ratios of 9.9 (≈1.1 × theoretical toluene total oxidation ratio), 18.2 (≈2.0 × theoretical ratio) and 31.2 (≈3.5 × theoretical ratio) were applied. The total gas flow rate was kept at 50 cm³/min giving toluene WHSV from 0.07 1/h to 0.06 1/h for feed ratios from 1.1 to 3.5. For reference, blank experiments without catalyst with all three O₂-toluene feed ratios were carried out.

In the oxidation experiment of CO, the reaction mixture was obtained by mixing CO + O₂ (2:1 mol/mol). In the water-gas shift experiment, the reaction mixture was obtained by mixing CO + H₂O + O₂ (2:0.14:1 mol/mol/mol). The total gas flow rate was kept at 50 cm³/min.

The composition of the gas flow from the reactor was analyzed by a mass spectrometer following the signals with mass/charge ratios of 2 (H₂), 15 (CH₄), 18 (H₂O), 28 (CO), 32 (O₂), 44 (CO₂), 78 (benzene) and 91 (toluene). Prior to the experiments, an experiment over pure ZrO₂ was performed scanning all mass signals from 5 to 130 to ensure that all relevant signals were monitored. The molar amounts of toluene and oxygen were quantified by single point calibration from the feed. The molar amount of water was quantified by single point calibration with a calibration gas. The calibration factors for CO₂, CO and H₂ (and an adjusted one for H₂O) were calculated in order to obtain fully closed mass balances at the steady state (at 600 °C) of the experiments. All gas mixtures were purchased from AGA (Table 1).

3. Results

All the experiments were carried out following the surface reaction in a temperature-programmed mode (TPSR, temperature-programmed surface reaction). In surface science studies, TPSR experiment is typically performed by pre-adsorbing one reactant on the catalyst surface and by constant feed of the other reactant while increasing the temperature. According to our previous findings, low-temperature-adsorbed form of toluene is not the catalytically relevant species and the formation of the key intermediate (surface benzyl species) from gas-phase toluene is an activated process [9]. Accordingly, pre-adsorption of one reactant is not adequate in our case and, thus, all the reactants were continuously fed to the catalyst while increasing the temperature. This

approach is expected to provide rich kinetic information on the reaction mechanism.

3.1. Catalyst comparison

The oxidation of toluene over ZrO_2 , $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ was carried out. The composition of the gas flow from the reactor for each component was analyzed by mass spectrometry.

3.1.1. Conversion of toluene and oxygen

In the temperature-programmed toluene oxidation experiments (toluene WHSV 0.07 1/h), toluene was fully converted over all ZrO_2 -based catalysts by 550 °C (Fig. 1). The conversion of toluene started around 300 °C over ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$, while over $\text{SiO}_2\text{-ZrO}_2$ notable toluene conversion was observed already around 250 °C (Fig. 1). Furthermore, in the reference experiment without catalyst (denoted as “Blank” in Fig. 1), toluene conversion was below 5% throughout the temperature ramp suggesting that thermal reactions have a minor contribution. The conversion of toluene over ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$ forms an S-curve as a function, whereas that of $\text{SiO}_2\text{-ZrO}_2$ clearly differed from those of ZrO_2 and $\text{Y}_2\text{O}_3\text{-ZrO}_2$.

Unlike the conversion of toluene, the conversion of oxygen was incomplete (80–90%) with 1.1 feed ratio at 600 °C (Fig. 1). Also, no more than 2% of oxygen was consumed in the reference experiment (denoted as “Blank” in Fig. 1). Furthermore, the conversion of oxygen over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ increased throughout the temperature ramp, while over ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ the conversion of oxygen first increased, then decreased and finally increased again with increasing temperature. The activity order of the catalysts can be evaluated from the conversion curves of toluene and oxygen in the temperature range from 200 °C to 550 °C. Over $\text{SiO}_2\text{-ZrO}_2$ both toluene and oxygen started to convert at lower temperatures than on the other catalysts suggesting that $\text{SiO}_2\text{-ZrO}_2$ was the most active catalyst in toluene oxidation, while $\text{Y}_2\text{O}_3\text{-ZrO}_2$ was the least active one (Fig. 1). By 550 °C all the catalysts were equally active as complete conversion of toluene had been reached.

3.1.2. Formation of products

In all toluene oxidation experiments over ZrO_2 -based catalysts, four products were detected: CO_2 , CO, H_2 and H_2O in accordance with our previous findings [9]. The temperature-programmed surface reaction (TPSR) profiles of the products are shown in Fig. 2. Over all the catalysts, the formation of CO_2 and H_2O first increased with increasing temperature but over ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ the formation curves peaked at around 450 °C, especially the CO_2 formation curve over $\text{SiO}_2\text{-ZrO}_2$ showed a clear maximum. The formation of CO and H_2 first increased with increasing temperature and then started to decrease over all the catalysts. The evolution of CO_2 , CO and H_2 started first with increasing temperature over $\text{SiO}_2\text{-ZrO}_2$ in accordance with the first consumption of both reactants over this catalyst. Furthermore, over $\text{SiO}_2\text{-ZrO}_2$ the TPSR profiles showed larger product amounts than over the other catalysts, also in accordance with its higher activity. Likewise, the peak areas in the product TPSR profiles over the least active catalyst, i.e., $\text{Y}_2\text{O}_3\text{-ZrO}_2$, were the smallest. The maximum CO and H_2 formation were detected around 470 °C. Over all the catalysts, the formation of CO was detected even at 600 °C. The formation of H_2 over ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ was seen as well at 600 °C, whereas over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ the formation of H_2 approached zero at 600 °C.

The formation of other products (besides CO_2 , CO, H_2 and H_2O) was negligible in the toluene oxidation experiments over ZrO_2 catalysts. Especially, no benzene was detected. This is advantageous as the presence of benzene is unacceptable if the product gas is targeted at Fischer-Tropsch synthesis, for example [6]. Furthermore, neither products of selective toluene oxidation, such as benzaldehyde, benzyl alcohol or benzoic acid, nor any other

reaction intermediates were detected. Similar results were published by Nag et al. [15] in a study of Mo oxides on different supports, where the formation of both benzaldehyde and benzoic acid over ZrO_2 was negligible but a small amount of benzene was detected. The formation of benzene derivatives that are also classified as tar would indicate that ZrO_2 -based catalysts convert one tar component to another which is not a desired characteristic for a gasification gas clean-up catalyst.

3.2. Temperature-programmed experiments of possible secondary reactions

To complement the toluene oxidation experiments, the interaction of CO and CO + H_2O mixture in the presence of oxygen over ZrO_2 -based catalysts was studied in order to investigate possible secondary reactions. Based on the two-step oxidation pathway suggested by Juutilainen et al. [5], the oxidation of carbon monoxide needs to be considered. The water-gas shift reaction was studied to assess ability of the catalysts to form hydrogen.

In the temperature-programmed CO oxidation experiment, the consumption of carbon monoxide and oxygen as well as the formation of CO_2 was observed over all the catalysts (Fig. 3). However, the temperature where CO oxidation started was different between the catalysts. Over pure ZrO_2 , oxidation of CO was detected at temperatures above 350 °C and over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ and $\text{SiO}_2\text{-ZrO}_2$ already at 275 °C. CO conversions above 60% were achieved at 600 °C over pure ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ whereas over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ the conversion of CO was 82% at 600 °C.

In the temperature-programmed water-gas shift (WGS, $\text{CO} + \text{H}_2\text{O} + \text{O}_2$) experiment, consumption of CO and H_2O was followed in the presence of oxygen. As far as we know, this is the first WGS experiment with a continuous feed over ZrO_2 -based catalysts and actually among all oxide materials. CO was consumed over all ZrO_2 -based catalysts above 350 °C (below in Fig. 3). In addition, oxygen was consumed and the formation of CO_2 was detected over all the catalysts. Consequently, the oxidation of CO into CO_2 took place over all ZrO_2 -based catalysts. CO conversions of above 50% were achieved at 600 °C over pure ZrO_2 and $\text{SiO}_2\text{-ZrO}_2$ while over $\text{Y}_2\text{O}_3\text{-ZrO}_2$ the conversion of CO was 81% at 600 °C. The formation of H_2 over the doped zirconias was negligible whereas over pure ZrO_2 a minor formation of H_2 was detected at 350–600 °C. Thus, it can be concluded that over pure ZrO_2 surface-mediated water-gas shift reaction took place at 350–600 °C.

3.3. Effect of oxygen amount

Three oxygen-toluene feed ratios of 9.9 ($=1.1 \times$ theoretical total oxidation ratio), 18.2 ($=2.0 \times$ theor. ratio) and 31.2 ($=3.5 \times$ theor. ratio) were applied for all ZrO_2 -based catalysts. The TPSR profiles of the components at the outlet of the reactor are shown for ZrO_2 in Fig. 4. Toluene was fully consumed above 500 °C with all three feed ratios. Oxygen, fed in surplus in all the experiments, was expectedly not completely consumed even at 600 °C. The achieved oxygen conversions over pure ZrO_2 at 600 °C were 82, 52 and 33% with feed ratios of 1.1, 2.0 and 3.5, respectively. For reference: in an experiment without catalyst, oxygen conversion was less than 1.4% with a feed ratio of 1.1.

With all the applied oxygen-toluene feed ratios, the TPSR profiles of each product (CO_2 , CO, H_2 and H_2O) showed uniform shapes (Fig. 4). Conversion curves of toluene and oxygen shifted towards lower temperatures and so did the maxima of product curves as a function of O_2 -toluene feed ratio, meaning that overall toluene oxidation as well as consecutive reactions were accelerated with increasing feed ratio. It is well-known that in temperature-programmed reduction (TPR) experiments, an increase in the amount of the reductant (such as H_2) shifts the rate maximum to

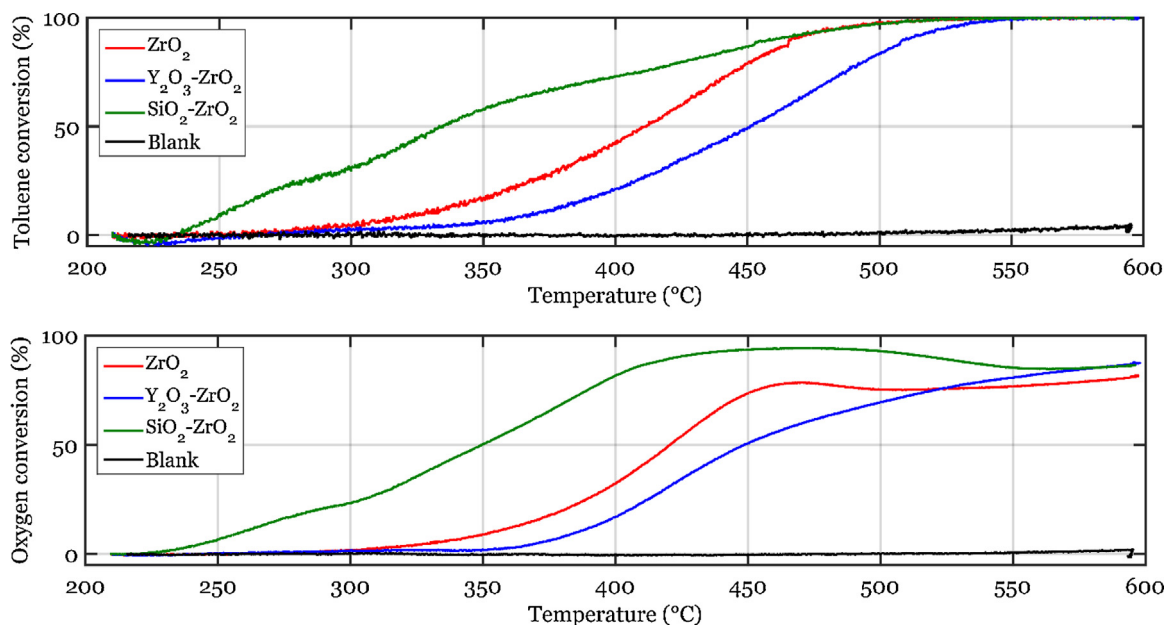


Fig. 1. The conversion of toluene (above) and oxygen (below) over ZrO_2 -based catalysts in the temperature-programmed oxidation of toluene (oxygen-toluene feed ratio: $1.1 \times$ theoretical total oxidation ratio, heating rate: $10^\circ\text{C}/\text{min}$).

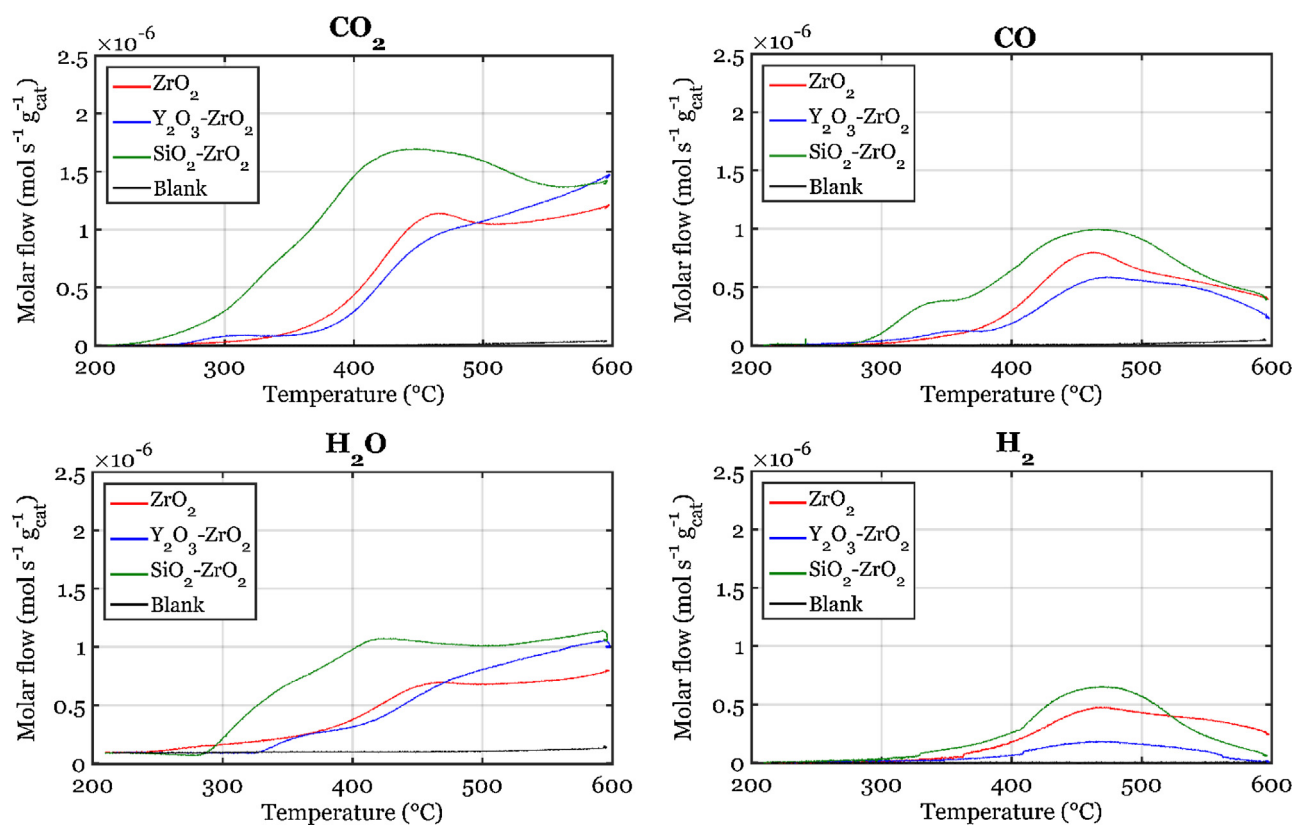


Fig. 2. TPSR profiles of product formation over ZrO_2 -based catalysts and without catalyst (blank) in the temperature-programmed oxidation of toluene (oxygen-toluene feed ratio: $1.1 \times$ theoretical total oxidation ratio, heating rate: $10^\circ\text{C}/\text{min}$).

lower temperature [16] and analogously in TPO experiments with an increasing O_2 amount [17]. For TPSR experiments, as implemented here, the maxima originate from the consecutive oxidation reactions with adsorbed surface species activating above 400°C . Increasing the fraction of oxygen in the feed decreases the temperature of a local rate maximum, as in TPO, suggesting that the overall rate of toluene oxidation is likely more sensitive to oxygen concen-

tration than to toluene concentration. Thus, the apparent reaction order is higher for oxygen than for toluene.

The TPSR profiles of the doped catalysts (Figs. S1 and S2 in Supplementary data) exhibited similar trends as those of pure ZrO_2 , but also contained more complicated features. Over the doped catalysts, the increasing feed ratio also shifted the maxima to lower temperatures.

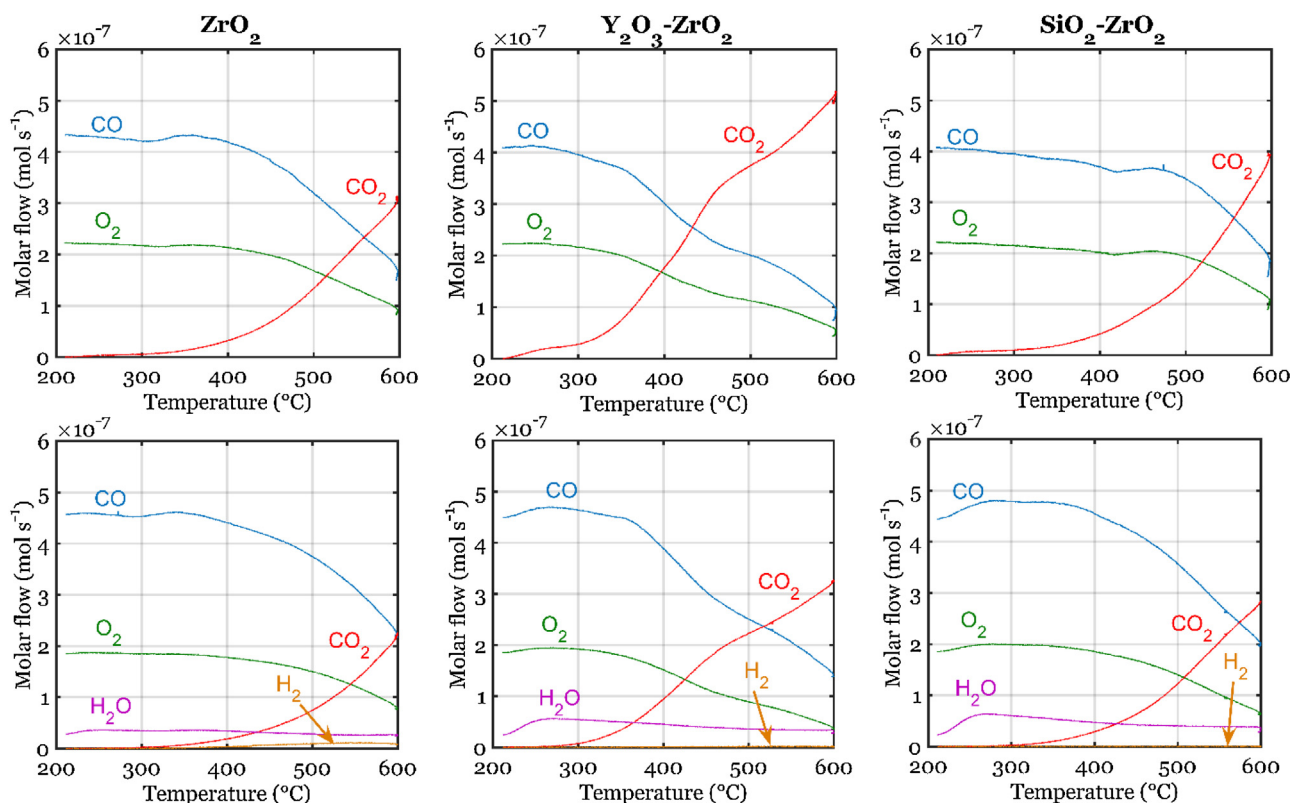


Fig. 3. Evolved gas compositions in the temperature-programmed experiments of possible secondary reactions: CO oxidation (above) and water-gas shift (below) over ZrO_2 -based catalysts.

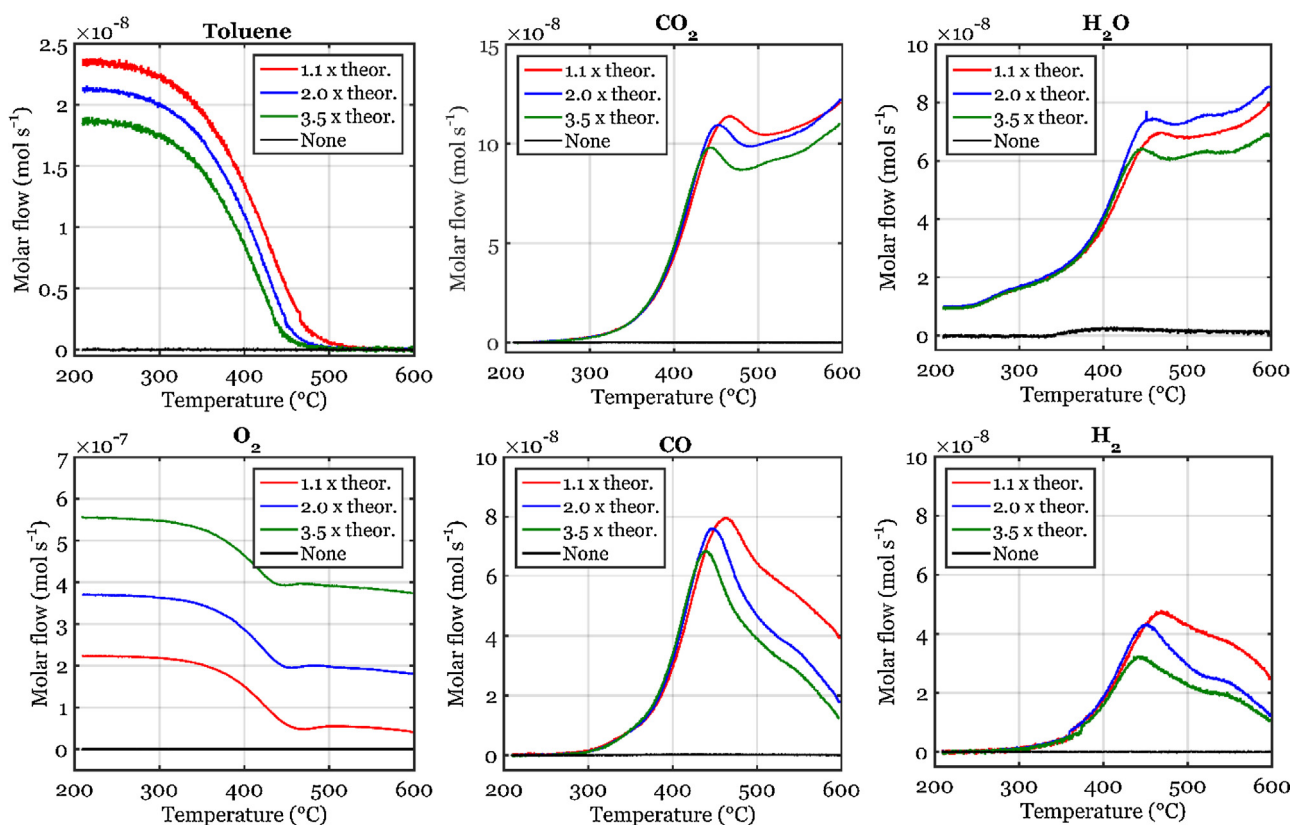


Fig. 4. TPSR profiles of the components at the reactor outlet with O_2 /toluene feed ratios of 1.1, 2.0 and 3.5 \times theoretical total toluene oxidation ratio over pure ZrO_2 . “None” refers to pure helium feed (no toluene or oxygen).

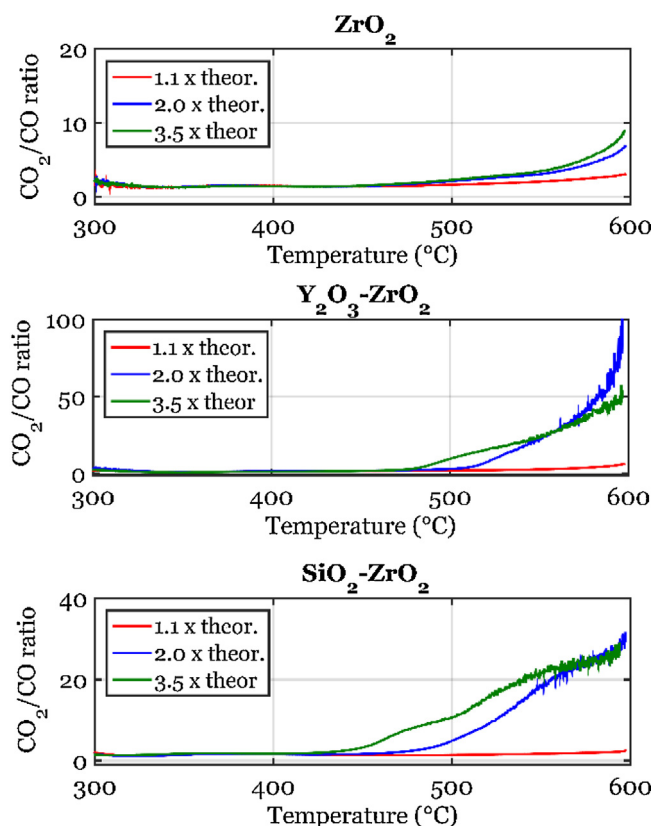


Fig. 5. Effect of O_2 -toluene feed ratio to the formation ratios of CO_2/CO over ZrO_2 -based catalysts with 1.1, 2.0 and 3.5 times theoretical total toluene oxidation ratio.

Over all the catalysts, the O_2 -toluene feed ratio clearly affected the distribution of products during the temperature-programmed toluene oxidation. The CO_2/CO ratio increased especially at higher temperatures when the oxygen amount was increased (Fig. 5). Over pure ZrO_2 , by increasing the feed ratio, i.e., increasing the oxygen amount, the CO_2/CO ratio increased at temperatures above 475 °C. Over Y_2O_3 - ZrO_2 , the temperature where the CO_2/CO ratio started to increase was the same as over pure ZrO_2 (around 475 °C), whereas over SiO_2 - ZrO_2 the ratio started to increase already at slightly lower temperatures (around 450 °C). Interestingly, over all the catalysts the CO_2/CO ratio was constant regardless of the feed ratio before it started to increase as a function of temperature. Over pure ZrO_2 , for example, the ratio of CO_2/CO was 1.3 (4:3) until 450 °C. This constant ratio over a range of conversion levels indicates that both carbon oxides are primary products of toluene oxidation.

Over pure ZrO_2 , the CO_2/CO ratio increased moderately with increasing oxygen amount and temperature (Fig. 5). CO_2/CO ratios of 2.9, 6.1 and 8.0 were observed over pure ZrO_2 at 600 °C with the feed ratios of 1.1, 2.0 and 3.5, respectively. Over Y_2O_3 - ZrO_2 , CO_2/CO ratio of 6.0 was achieved at 600 °C with the lowest feed ratio, while over SiO_2 - ZrO_2 the CO_2/CO ratio was 2.4. When the oxygen amount was further increased (from feed ratio of 2.0–3.5) over the doped zirconias, the CO_2/CO ratio increased until 550 °C. At this temperature, the amount of CO formed over the doped catalysts approached zero and the ratio of CO_2/CO became meaningless. Hence, the general trend over all the ZrO_2 -based catalysts is that below a certain combination of temperature and feed ratio, the ratio of CO_2/CO remains constant, after which it continuously increases. This implies that for a range of conversions, CO_2 and CO are primary products whereas above certain combination of temperature and feed ratio a part of detected CO_2 results from the oxidation of CO.

The H_2O/H_2 ratio (not shown) increased with increasing temperature over all the catalysts. However, over ZrO_2 and SiO_2 - ZrO_2

with the feed ratio of 1.1, the increasing of the H_2O/H_2 ratios with increasing temperature were moderate reaching values of 3 and 11, respectively, at 600 °C. Over Y_2O_3 - ZrO_2 with the feed ratio of 1.1, the H_2O/H_2 ratio increased dramatically with increasing temperature above 525 °C. In addition, the H_2O/H_2 ratio increased with increasing O_2 -toluene feed ratio from 1.1 to 2.0 over all the catalysts. Over pure ZrO_2 with the feed ratio of 2.0, highest H_2O/H_2 ratio was around 6 at 600 °C. Over the doped catalysts with the feed ratio of 2.0, the H_2O/H_2 ratio increased dramatically because the amount of H_2 started to approach zero. As in the case of the CO_2/CO ratio, the general trend over all the ZrO_2 -based catalysts is that the H_2O/H_2 ratio increased with the increasing temperature and oxygen amount. As a result, it can be concluded here as well that less H_2 and more H_2O is formed when more oxygen is available.

4. Discussion

4.1. Toluene oxidation activity

Toluene oxidation over ZrO_2 -based gasification gas clean-up catalysts was studied from 200 °C to 600 °C by temperature-programmed experiments. Toluene was fully converted over all ZrO_2 -based catalysts by 550 °C. The activity order of the catalysts was evaluated between 200 °C and 550 °C and it was found to decrease in the order of SiO_2 - ZrO_2 > ZrO_2 > Y_2O_3 - ZrO_2 . Comparing the toluene conversion at 450 °C to those obtained by Labaki et al. [13] in steady-state toluene oxidation experiments over ZrO_2 , a significant difference can be observed. In this work, a toluene conversion of 79% was achieved at 450 °C, while Labaki et al. [13] reported a toluene conversion of only ~32% over pure ZrO_2 . The explanation for the lower toluene conversion over pure ZrO_2 reported by Labaki et al. [13] could be their much higher toluene WHSV of 3.2 1/h (calculated from [13]) compared to this work (0.07 1/h). With a much higher toluene WHSV, much lower conversion is expected.

In the case of Y_2O_3 - ZrO_2 , the conversion of toluene at 450 °C in this work was 49% whereas a conversion of 63% was obtained by Labaki et al. [13] despite their higher WHSV. In toluene oxidation, as well as in the oxidation of other hydrocarbons, such as methane [18] or propene [13], the activity of ZrO_2 should be increased by the addition of Y_2O_3 . By contrast in this work, lower activity was observed over Y_2O_3 - ZrO_2 (49% at 450 °C) than over pure ZrO_2 (79% at 450 °C) throughout the studied temperature range. Water, being a minor impurity, could have affected the activity of Y_2O_3 - ZrO_2 . As was suggested by Zhu et al. [19], the active surface sites of Y_2O_3 - ZrO_2 are partially blocked by molecularly adsorbed water. However, in gasification gas cleaning the gas from the gasifier always contains a high amount of water vapor (around 12 vol-%, calculated from [7]).

When the toluene oxidation activities of ZrO_2 -based catalysts obtained in this work are compared to those within the gasification gas mixture over monoliths [7], a notable difference is observed. Complete toluene conversions were obtained at 600 °C over ZrO_2 -based catalysts in this work (Figs. 1 and 2) while toluene conversions of only 50, 35 and 10% over ZrO_2 , Y_2O_3 - ZrO_2 and SiO_2 - ZrO_2 , respectively, were observed in gasification gas cleaning at 600 °C [7]. The monolithic catalysts used in [7] were prepared from the powders used in this work. The toluene WHSV values of the experiments differ from each other (0.07 1/h in this work and 0.81 1/h calculated from [7]). With a higher toluene WHSV, lower conversion is expected but the considerably lower toluene conversions obtained in the presence of the synthetic gasification gas mixture could also be explained by possible mass transfer limitations in the monoliths. Furthermore, the presence of other gas components, such as CO, H_2O , CO_2 , H_2 , CH_4 , C_2H_4 and NH_3 could have

Table 2
Surface properties of ZrO₂-based gasification gas clean-up catalysts [7].

Catalyst	Specific surface area (m ² g ⁻¹)	Amount of basic sites (μmol g ⁻¹)	Amount of acidic sites (μmol g ⁻¹)
ZrO ₂	24	84	22
Y ₂ O ₃ -ZrO ₂	53	146	36
SiO ₂ -ZrO ₂	92	49	78

an effect on the activity of ZrO₂-based catalysts. The highest difference between measured toluene conversions in toluene oxidation (100% at 600 °C) and in gasification gas cleaning (10% at 600 °C) [7] can be observed over SiO₂-ZrO₂. It is possible that over this catalyst the other gas components affect the toluene oxidation activity the most. In addition, the lower activity of Y₂O₃-ZrO₂ in toluene oxidation, when a small amount of water is present, as discussed above, suggests that the other gas components indeed affect the activity of these catalysts. The other gas components can affect the catalyst performance by means of product inhibition, competitive oxidation reactions of other hydrocarbons and poisoning the active sites.

The surface properties of ZrO₂, Y₂O₃-ZrO₂ and SiO₂-ZrO₂ were studied in our earlier work [7] and have been collected to Table 2. The specific surface areas of the catalyst samples were re-measured after the sample preparation (pelletization, crushing and sieving), but the values were the same as reported in [7]. When the specific surface areas of the catalysts were taken into account, the order of product formation intensity changed. For example, the most intense CO formation (per gram of catalyst) was observed over SiO₂-ZrO₂, which also has the highest specific surface area whereas the specific surface area of ZrO₂ is the lowest. When the formation of CO is calculated per specific surface area, CO formation over ZrO₂ becomes the most intense one. It can be concluded that the density of active sites over ZrO₂ per m² must be the highest of these catalysts.

Toluene oxidation activity was shown to decrease in the order of SiO₂-ZrO₂ > ZrO₂ > Y₂O₃-ZrO₂ between 200 °C and 500 °C. The highest amount of acidic surface sites was measured on SiO₂-ZrO₂ and lowest on pure ZrO₂ (Table 2). Consequently, high acidity correlates with toluene oxidation activity. The acidity of catalysts has been related to their activity in toluene total oxidation, e.g., several metal oxides supported on zeolite obey this behavior [21]. In contrast, high acidity of ZrO₂-based catalysts in tar oxidation within the gasification gas mixture has previously been reported to be unfavorable [7]. The amount of basic surface sites decreased in the order of Y₂O₃-ZrO₂ > ZrO₂ > SiO₂-ZrO₂ (Table 2), which correlates with the reverse activity order in toluene oxidation giving the impression that basicity could be even disadvantageous. Yet again, the increasing amount of basic surface sites seemed to correlate with high gas cleaning activity [7]. It can be concluded arising from this that the active sites for toluene oxidation cannot solely be explained by their acidic or basic nature. Similarly, Busca [22] has also stated that basicity of vanadia-based selective oxidation catalysts has nothing to do with their ability to activate toluene or other methylaromatics.

4.2. Formation of CO and H₂

In all toluene oxidation experiments over ZrO₂-based catalysts, four products were detected: CO₂, CO, H₂ and H₂O. The most substantial finding is that ZrO₂-based catalysts are indeed able to convert toluene also into valuable synthesis gas components (CO and H₂). The formation of CO in toluene oxidation has been observed previously over ZrO₂-based catalysts. For example, the results of Labaki et al. [13] showed that 30% of the carbon-containing oxidation products was CO at temperatures of 400 and 450 °C for pure ZrO₂ and 5 mol-% Y₂O₃-ZrO₂ [13], while in this

work values of 24% and 14% over ZrO₂ and Y₂O₃-ZrO₂, respectively, were obtained at 600 °C. Far more interesting from a gasification gas cleaning point of view is the hydrogen share of all the products, being 7.5 mol-% for ZrO₂, 0.1 mol-% for Y₂O₃-ZrO₂ and 2.2 mol-% for SiO₂-ZrO₂ at 600 °C. The formation of H₂ in toluene oxidation experiments of Labaki et al. [13] was not reported.

Interestingly, the formation of all four products (CO₂, H₂O, CO and H₂) over ZrO₂ and Y₂O₃-ZrO₂ has been reported by Zhu et al. [18] in the oxidation of methane. Although the H/C ratio of methane is much higher than that of toluene, the formation of incomplete oxidation products (CO and H₂) seems to be in common in the oxidation of these two hydrocarbons over ZrO₂ and Y₂O₃-ZrO₂. Zhu et al. [23] showed that in methane oxidation over ZrO₂ and Y₂O₃-ZrO₂ formation of CO and H₂ occurred via decomposition of two oxygen-containing intermediate surface species (adsorbed formaldehyde and surface formate), whereas our previous spectroscopic results indicated that the intermediate in toluene oxidation contains no oxygen (a surface benzyl species) [9]. An oxygen-containing surface species, namely benzoate species, was also observed during toluene oxidation but it was suggested to be a spectator species due its high stability [9]. Thus, it seems unlikely that the formation of CO and H₂ in toluene oxidation could be explained by the decomposition of oxygen-containing surface species.

A small amount of hydrogen was detected in the water-gas shift reaction over pure ZrO₂ (Fig. 3). It is possible that the formation of H₂ in toluene oxidation is related to the surface chemistry of ZrO₂, i.e., the involvement of hydroxyl groups of ZrO₂. For example, a recent study on CO surface reaction experiments (CO-TPSR) over calcined, and then reduced and/or hydrated ZrO₂ samples showed H₂ evolution at temperatures above 300 °C regardless of the pre-treatment [24]. H₂ was suggested to be formed via surface reaction between formates and multicoordinated hydroxyl groups on the ZrO₂ surface [24]. However, over the doped catalysts water-gas shift activity (Fig. 3) was not detected at the temperature range of 200–600 °C while in the toluene oxidation experiments (Fig. 2), hydrogen formation was evident. As WGS reaction plays only a minor role over pure zirconia and is negligible over the doped zirconias, hydrogen is clearly a primary product of toluene decomposition under oxygen.

4.3. Effect of oxygen

The increasing O₂-toluene feed ratio, i.e., the oxygen amount, increased the ratio of CO₂/CO over all the catalysts with increasing temperature. The strongest effect of the oxygen amount on the CO₂/CO ratio was seen over Y₂O₃-ZrO₂ whereas the weakest effect was seen over ZrO₂. The ratio of CO₂/CO was constant up to temperatures around 450 °C (Fig. 5) although significant conversion of toluene as well as formation of products were already observed over all the catalysts at much lower temperatures (Fig. 1). All catalysts showed CO oxidation activity (Fig. 3), implying that in toluene oxidation the formed CO was converted into CO₂ in a secondary reaction. The fact that the ratio of CO₂/CO was constant until 450 °C suggests that this secondary reaction took place only above this temperature, disagreeing with the proposal by Juutilainen et al. [5] where the only primary products were CO and water, whereas CO₂

was only a secondary product. We claim that both carbon oxides are primary products in toluene oxidation over these catalysts.

The $\text{H}_2\text{O}/\text{H}_2$ ratio increased with increasing temperature and oxygen amount over all the catalysts. Even though the H_2 oxidation activity of these catalysts was not measured, it can be suggested, based on the similarities in the product formation ratios (CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$), that H_2 is oxidized into H_2O in a secondary reaction.

The effect of an increasing oxygen amount to naphthalene oxidation over pure ZrO_2 has been studied by Rönkkönen et al. [8] applying a synthetic gasification gas mixture. Their results indicated that with the increasing oxygen amount, conversion of both CO and H_2 increased [8]. However, the comparison is not straightforward since neither CO nor H_2 was fed in this work. Moreover, the tar model compound used in our work (toluene) was different than that used by Rönkkönen et al. [8] (naphthalene). Nevertheless, both studies clearly indicate that increasing the oxygen amount causes the oxidation of valuable gas components, i.e., CO and H_2 . Based on these studies, the gasification gas cleaning over ZrO_2 -based catalysts is recommended to be carried out using oxygen amounts that correspond closely to the stoichiometric tar total oxidation amount.

5. Conclusions

Temperature-programmed oxidation of toluene from 200 °C to 600 °C was studied over ZrO_2 , Y_2O_3 - ZrO_2 and SiO_2 - ZrO_2 . Over all the catalysts, toluene was completely consumed at temperatures above 550 °C into four products: CO_2 , H_2O , CO and H_2 . All four compounds are primary reaction products, as carbon oxides are formed in a constant proportion (CO_2 to CO = 4:3) over a large temperature and conversion window. Hydrogen is also formed directly from toluene since WGS reaction was hardly detected. The formation of incomplete oxidation products (CO and H_2) as primary toluene oxidation products shows that these catalysts are also able to convert toluene into valuable synthesis gas components. All the catalysts showed formation of CO and H_2 at temperatures between 200 °C and 550 °C. When either the reaction temperature or oxygen concentration was increased above a certain threshold value, CO and H_2 diminish among the reaction products in a direct correlation with the increase of the total oxidation products, clearly indicating that these incomplete oxidation products (or their common surface intermediate) undergo total oxidation. There exists a range of conditions where preferential toluene decomposition is possible with simultaneous protection of syngas. This calls for process optimization based on quantitative understanding of toluene oxidation kinetics.

The multiresponse reaction data collected in this work was subsequently subjected to transient kinetic modeling. Therefore, a surface reaction mechanism of toluene oxidation is presented in Part B.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.06.014>.

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